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# The relationship between regional SO<sub>2</sub> emissions and downwind aerosol sulfate concentrations in the northeastern US

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## Abstract

Our research group has been continuously measuring aerosol sulfate at Whiteface Mountain, New York, since 1979 and at Mayville, New York, since 1984. Monthly aerosol SO<sub>4</sub><sup>2-</sup> concentrations for these sites are reported here through 1997. Seasonal and long-term profiles of SO<sub>4</sub><sup>2-</sup> are presented along with SO<sub>2</sub> concentrations. As these sites are directly downwind of the high SO<sub>2</sub> emission region in the Midwestern United States and the same sampling and analytical protocol has been maintained, they are ideally suited to evaluate long-term trends. The recent reductions in SO<sub>2</sub> emissions in response to provisions of the 1990 Clean Air Act provide an excellent opportunity to evaluate the sulfur source–receptor relationship. A linear relationship is demonstrated between aerosol SO<sub>4</sub><sup>2-</sup> and total sulfur (S<sub>T</sub>, sum of S present as SO<sub>4</sub> and SO<sub>2</sub>) concentrations at these sites and SO<sub>2</sub> emissions upwind in the Midwest. This is the most direct evidence to date that deposition of sulfur in the Northeast is linearly related to upwind SO<sub>2</sub> emissions. The results support the possibility of using the ratio of SO<sub>4</sub><sup>2-</sup>/SO<sub>2</sub> emissions to develop an empirical source–receptor relationship for the region. © 2000 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Whiteface Mountain, 1.5 km above mean sea level, amsl, is located in the Adirondack Region of New York State. Although the area is relatively remote from major urban/industrial areas, it is strongly stressed by acid deposition primarily from sulfuric acid and its salts (e.g. NAPAP, 1991). Many studies have demonstrated that aerosol SO<sub>4</sub><sup>2-</sup> (expressed simply as SO<sub>4</sub>) concentrations at this site are highly variable (< 1–50 µg m<sup>-3</sup>), and that it is primarily influenced by transport from distant sources west and southwest of the site (Parekh and Husain, 1982; Husain et al., 1984; Husain and Dutkiewicz, 1990).

Atmospheric SO<sub>4</sub> is primarily produced from the oxidation of SO<sub>2</sub>. In the northeastern United States, fossil fuel combustion is the primary source of SO<sub>2</sub> emissions. Both gas- and aqueous-phase reactions oxidize SO<sub>2</sub> to SO<sub>4</sub>. Aqueous-phase oxidation, though more sporadic than gas-phase oxidation, is much more rapid. While gas-phase oxidation only occurs in day time with a rate around 1% per hour (Newman, 1981), aqueous oxidation in a typical cloud can occur at 1000% per hour (Pandis and Seinfeld, 1989). Thus, the fraction of S as SO<sub>2</sub> depends on the distance from the source. Anthropogenic emission sources of SO<sub>2</sub> in the United States are monitored by the USEPA (e.g., USEPA, 1996). The highest density of these sources is located along the Ohio River Valley (ORV) and the lower Great Lakes (GLK). Emissions from Ohio and Indiana rank first and second among the states, and the combined emissions from MN, WI, IL, IN, MI, OH, WV, KY, and western PA contributed 38% of the national emissions in 1995

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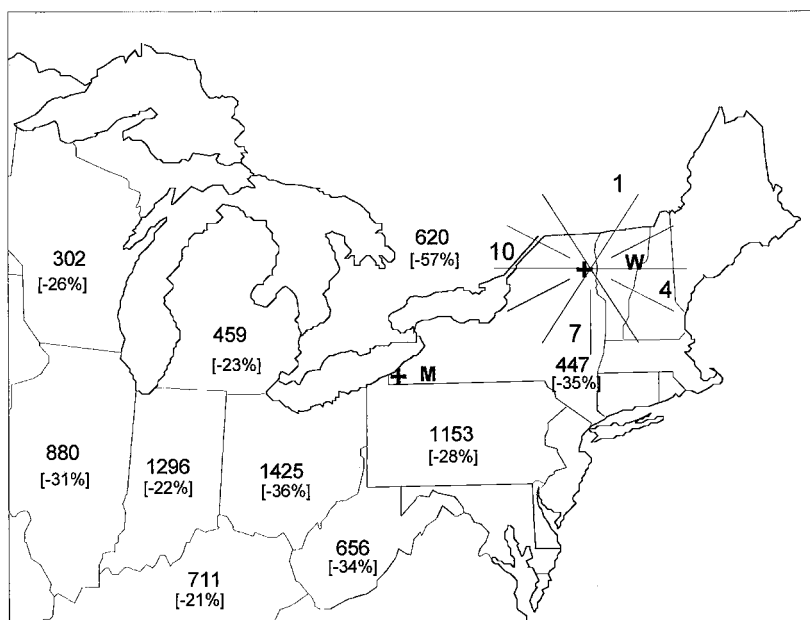


Fig. 1. Map showing the location of Mayville (M) and Whiteface Mountain (W). Also shown are 1995 SO<sub>2</sub> emissions (10<sup>3</sup> metric tons per day) for New York and upwind Midwest states (USEPA, 1996) and Ontario Canada (Environment Canada, 1995,1997). Also shown is the % change in emissions relative to 1985 (shown in [ ]). The area around Whiteface Mountain is shown divided into twelve 30° sectors used for trajectory analysis of the data as explained in the text.

(USEPA, 1996). We will refer to this region simply as Midwest. While SO<sub>2</sub> emissions in the Midwest have been decreasing very slowly since the late 1970s, a dramatic decrease occurred in 1995. Fig. 1 shows 1995 emission levels in eastern United States and Ontario, Canada along with the percent change in emissions relative to 1985 levels. There is a 21–36% decrease in the emissions from the Midwestern states and most of this occurred during 1995. The emissions for Ontario decreased by 57%, however, there has been a more steady decrease there since 1990. These large reductions provide a unique opportunity to “field test” our present understanding of atmospheric sulfur chemistry and transport.

Husain and Dutkiewicz (1990) summarized aerosol SO<sub>4</sub> concentrations measured at Whiteface Mountain and at a site in western-most New York near the Midwest, Mayville (Fig. 1), through 1988. Air trajectories and regional elemental ratios were used to relate high SO<sub>4</sub> concentration at Mayville and Whiteface Mountain to air masses that originated in the Midwest. Nearly two-thirds of the SO<sub>4</sub> at Whiteface Mountain and three quarters at Mayville were related to emissions from the Midwest. As reported in Husain et al. (1998), annual mean concentrations of SO<sub>4</sub> at Whiteface Mountain and Mayville are strongly correlated ( $r^2 = 0.76$ ), consistent with the dominance from a common source region. Brook et al. (1997) also found good temporal correlations

between SO<sub>4</sub> concentrations at many of their sites in Ontario, Quebec and the Maritime provinces. For sites at Egbert, Sutton, and Kejimikujik (aligned west to east), improved correlation was found if daily SO<sub>4</sub> concentrations were off-set to compensate for the time it takes air-masses to move from Ontario to the Maritimes. Similar to Mayville and Whiteface Mountain, SO<sub>4</sub> concentrations at the Canadian sites appear to be strongly influenced by SO<sub>2</sub> emission in the Midwest/Great Lakes regions.

Recently, Husain et al. (1998) demonstrated a linear relationship between SO<sub>2</sub> emissions in these Midwest states and SO<sub>4</sub> concentrations at Mayville and Whiteface Mountain. Over the 18-yr span of data reported for Whiteface Mountain, the ratio of SO<sub>4</sub> concentration to Midwest SO<sub>2</sub> emissions had a mean and 1 sigma deviation of  $0.110 \pm 0.014 \mu\text{g m}^{-3} \text{ SO}_4$  per  $10^3$  metric tons of SO<sub>2</sub> emissions per day, while over the 13-yr span at Mayville the ratio was  $0.230 \pm 0.014 \mu\text{g m}^{-3} \text{ SO}_4$  per  $10^3$  metric tons of SO<sub>2</sub> emissions per day. Thus, over these long-time spans where both quantities have changed by at least a factor of 2, this ratio has only a 13% standard deviation at Whiteface Mountain and a 5% deviation at Mayville. A similar relationship was found for total sulfur (S<sub>T</sub>, sum of S as aerosol SO<sub>4</sub> and SO<sub>2</sub>). This is a remarkable observation. Space constraints, however, limited the scope of the data presented in Husain et al. (1998). In this paper monthly mean SO<sub>4</sub> and

$S_T$  data from both Mayville and Whiteface Mountain are reported through 1997. Discussion of the data here are focused on seasonal trends, relationship with air trajectories, and comparison of these results with upwind  $SO_2$  emission trends.

## 2. Experimental

### 2.1. Sampling

Daily high-volume aerosol samples were collected on  $20 \times 25$  cm Whatman 41 filters at Whiteface Mountain ( $44^\circ 15'N$ ,  $73^\circ 51'W$ , 1.5 km amsl) and Mayville ( $42^\circ 18'N$ ,  $79^\circ 30'W$ ), New York (Fig. 1). Continuous sampling at Whiteface Mountain began in June, 1978 but it was interrupted for some time in 1980 and 1982. Aerosol sampling at Mayville was first conducted on a campaign basis in 1981 and continuous sampling began in June of 1983. Description of the sites, filters and sampling may be found elsewhere (Husain and Dutkiewicz, 1990; Husain et al., 1984).  $SO_2$  concentrations were provided from continuous monitoring sites operated by the New York State Department of Environmental Conservation (William Delaware, personal communication). The data used for Mayville is from nearby Westfield, NY, a rural area 10 km west of Mayville adjoining Lake Erie, while the data at Whiteface Mountain is recorded with a Thermo-Environmental Model 43S pulsed-fluorescence analyzer which has a detection limit of 0.1 ppb.

### 2.2. Analytical methods

Sulfate concentrations were determined in warm water extracts from either 10.1 or 20.2 cm<sup>2</sup> of each filter using ion chromatography (IC) since 1981 (Husain et al., 1984). Analytical performance and absence of interferences were controlled by analyzing digestates of blank filters, standard  $SO_4$  solution, samples spiked with known  $SO_4$  concentrations, and quality control samples provided by a separate laboratory. Blank values were  $< 0.01$  mg  $SO_4/l^{-1}$  and recoveries for all quality-control samples were 90–105%. At least 5% of the samples were analyzed in duplicate extractions which have maintained an RSD of  $< \pm 5\%$ . The overall analytical uncertainty for  $SO_4$  is  $\pm 7\%$  for most samples.

### 2.3. Air trajectories computations

An air trajectory, as used here, refers to the path that an air parcel has taken to reach a certain point in space and time. Several different computer models are available but each computes the latitude and longitude of an air parcel at a fixed interval backward in time. Prior to 1992 four air trajectories with ending times of 0200, 0800, 1400, and 2000 h EST were computed for each day at the two

sites using the ATAD BAT model (Hefter, 1983). This model uses wind fields, averaged between 300 and 3000 m, obtained from radiosonde data collected 4 times daily around North America. The model computed the position of the air mass at 3 h intervals. As data for this model was no longer supported after 1992, we switched to the NOAA Hybrid Single-Particle Lagrangian Integrated Trajectory model (HY-SPILT 3) (Draxler, 1992) driven by meteorologic data archived from the National Meteorologic Center's Nested Grid Model. The starting height was set to 1.5 km, the height of Whiteface Mountain summit and roughly in the middle of the layer that was averaged with the ATAD model and we allowed the model to adjust the height of the particle based on meteorologic conditions. The same four ending times were used, however, the HY-SPLIT model was run with 2-h time steps. We ran a month of air trajectories at both Whiteface Mountain and Mayville during July, 1991 with both models. While individual trajectories usually compared well, at times, there were substantial differences in the air mass pathways. However, if the data for the month are collectively used to apportion the air masses into the twelve  $30^\circ$  sectors given in Fig. 1 using the procedures outlined by Parekh and Husain (1982), the sector fractions from the two models had a relative difference of less than 5% for all 12 sectors at Whiteface Mountain, and only the result for one of the sectors at Mayville differed by more than 5%.

## 3. Results

### 3.1. Aerosol sulfate

Table 1 gives monthly and annual mean  $SO_4$  concentrations at Whiteface Mountain from 1979 to 1997 and at Mayville from 1981 to 1997. To make it easier to directly compare  $SO_4$  and  $SO_2$  concentrations, all quantities are expressed in ppb. For aerosol  $SO_4$ , 1 ppb equals  $3.93 \mu g m^{-3}$ , STP. Daily concentrations are available from the authors. At Whiteface Mountain an average of 287 days were sampled per year compared to 326 at Mayville. Husain et al. (1998) discussed the details of the sample set, the impact of missing data on the annual means, and compared annual mean  $SO_4$  concentrations at these sites through 1996 to  $SO_2$  emissions in the upwind Midwestern states. Relatively small changes in  $SO_4$  concentrations were noted through 1994 (long-term mean) at both sites, but large decreases occurred in 1995 and 1996. The means computed in Table 1 and the discussions herein reflects this observation.

For 1981–1994 the highest mean monthly concentrations were 2.39 ppb at Whiteface Mountain, and 3.54 ppb at Mayville. The highest concentration at both sites occurred in August and the lowest in November–January. During the first-quarter (1981–1994)  $SO_4$  concentration

Table 1  
Monthly mean aerosol SO concentrations<sup>a</sup> at Mayville and Whiteface Mountain, NY

	1979	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	Mean	
																			1981–1994 ± sigm <sup>a</sup>	1995–97
Whiteface Mountain																				
JAN	0.28	0.38		0.24	0.71	0.25	0.38		0.46	0.33	0.28	0.35	0.15	0.22	0.26		0.19	0.14	0.33 ± 0.1	0.16
FEB	0.43	0.46		0.46	0.56	0.59	0.41	0.25	0.41	0.48	0.36	0.36	0.17	0.31			0.11	0.26	0.40 ± 0.1	0.19
MAR	0.79	0.46		0.46	0.38	0.31	0.56	0.56	0.56	0.56	0.51	0.33	0.25	0.53		0.39	0.32	0.19	0.45 ± 0.1	0.30
APR	0.84	0.53		0.33	0.51	0.99	0.43	0.41	0.56	0.64	0.97	0.79	0.28	0.41		0.23	0.37	0.34	0.57 ± 0.2	0.31
MAY	1.12	0.89		0.71	0.74	0.94	0.94		0.76	0.94	0.61	0.64	0.38	0.79	0.37	0.21	0.44	0.45	0.73 ± 0.2	0.36
JUN	2.19	1.37		2.11	1.12	0.66			0.79	0.92	1.45	1.12	1.09	0.53	1.12	0.39	0.76	0.63	1.12 ± 0.4	0.59
JUL	2.52	1.12		1.22	1.70	0.87	1.09	2.29	1.88	1.50	1.02	1.50	0.53	0.94	1.59	1.63	0.53	0.85	1.33 ± 0.5	1.00
AUG	0.89	1.96	0.76	1.65	2.39	1.32	1.81	1.09	1.65	1.07	1.35		2.01	1.48	1.70	0.73	1.01	0.99	1.56 ± 0.4	0.91
SEP	1.04	0.69		1.32		1.83	0.79	0.97	0.97	1.55		0.51			0.67	0.31	0.37	0.44	1.04 ± 0.5	0.37
OCT	1.04			0.46	0.69	0.43	0.36	0.53	0.56	0.94		1.02	0.43		0.36	0.48	0.24	0.34	0.58 ± 0.2	0.35
NOV	0.56			0.31	0.23			0.28	0.34	0.36	0.33	0.31	0.19		0.25		0.08	0.15	0.29 ± 0.1	0.11
DEC	0.31	0.36		0.36	0.22	0.36		0.24	0.25	0.09	0.18	0.23	0.20	0.18	0.21	0.09	0.12	0.28	0.24 ± 0.1	0.16
1st quarter <sup>b</sup>	0.50	0.43		0.39	0.55	0.38	0.41	0.38	0.47	0.46	0.38	0.35	0.19	0.35		0.25	0.21	0.20	0.40 ± 0.1	0.22
2nd quarter <sup>b</sup>	1.38	0.93		1.05	0.79	0.87	0.69	0.75	0.70	0.83	1.01	0.85	0.59	0.58	0.75	0.28	0.52	0.47	0.80 ± 0.1	0.42
3rd quarter <sup>b</sup>	1.48	1.26		1.40	1.71	1.34	1.20	1.50	1.50	1.37	1.14	1.19	1.20	1.15	1.32	0.89	0.64	0.76	1.33 ± 0.2	0.76
4th quarter <sup>b</sup>	0.64	0.41		0.37	0.40	0.34	0.29	0.35	0.38	0.46	0.36	0.52	0.27	0.35	0.27	0.23	0.15	0.26	0.37 ± 0.1	0.21
Year <sup>b</sup>	1.00	0.76		0.80	0.86	0.73	0.69	0.74	0.77	0.78	0.72	0.73	0.56	0.61	0.66	0.41	0.38	0.42	0.72 ± 0.1	0.40
Mayville																				
JAN					1.27	1.09	1.09	1.09	0.99	0.97	0.94	0.71	0.90		1.05	0.53	0.73	0.60	1.01 ± 0.1	0.62
FEB					1.20	1.27	1.22	0.89	1.15	0.87	0.89	0.82	0.74	1.12	1.10	1.53	0.63	0.77	1.02 ± 0.2	0.98
MAR					1.20	0.76	1.27	0.92	1.12	1.32	1.20	0.69	0.69	1.34	1.32	1.27	0.87	0.58	1.08 ± 0.3	0.91
APR					1.09	1.73	0.94	0.99	1.15	1.11	1.49	1.11	0.98	1.00	0.87	0.40	0.70	0.65	1.13 ± 0.3	0.59
MAY					1.09	1.50	1.63	2.16	1.73	1.63	1.14	1.74	1.32	1.20	0.89	0.10	0.81	0.49	1.46 ± 0.4	0.47
JUN					1.76	1.35	1.48	1.32	1.53	2.75	1.85	1.35	1.72	1.55	1.81	1.65	1.58	1.37	1.79 ± 0.5	1.53
JUL	2.72	1.73		3.03	2.57	2.01	1.76	3.31	3.05	2.53	2.15	2.93	1.17	2.32	2.67	1.54	1.20	1.49	2.38 ± 0.6	1.41
AUG	3.08	1.98			2.21	2.39	2.09	1.60	2.62	2.80	3.54	2.65	1.76	2.38	2.77	1.77	1.96	1.18	2.53 ± 0.6	1.64
SEP					1.45	2.26	2.04	1.81		1.39	1.70	1.51		1.10	1.53	1.12	1.18	1.35	1.68 ± 0.4	1.22
OCT					1.81	0.84	1.12	0.92	0.84	1.67	1.08	1.09	0.84	0.92	0.76	1.37	0.83	1.17	1.07 ± 0.3	1.12
NOV					0.99	0.89	1.02	1.07	1.02	0.71	1.01	0.82	0.86	0.99	0.59	0.80	0.51	0.73	0.89 ± 0.2	0.68
DEC					0.81	1.07	1.40	0.87	0.70	0.94	0.60	0.60	0.68	0.96	0.79	0.57	0.57	0.59	0.87 ± 0.2	0.58
1st quarter <sup>b</sup>					1.22	1.04	1.20	0.97	1.09	1.06	1.01	0.74	0.78	1.15	1.16	1.11	0.74	0.65	1.04 ± 0.2	0.83
2nd quarter <sup>b</sup>					1.31	1.53	1.35	1.49	1.47	1.83	1.49	1.40	1.34	1.25	1.19	0.72	1.03	0.84	1.42 ± 0.2	0.86
3rd quarter <sup>b</sup>	2.49	1.80		2.71	1.89	2.14	2.17	2.24	2.45	2.24	2.46	2.36	1.54	1.93	2.32	1.48	1.44	1.34	2.20 ± 0.3	1.42
4th quarter <sup>b</sup>				0.94	1.26	0.87	1.18	0.95	0.85	1.11	0.89	0.84	0.79	0.96	0.71	0.91	0.64	0.83	0.95 ± 0.2	0.79
Year <sup>b</sup>					1.42	1.40	1.47	1.41	1.46	1.56	1.46	1.33	1.11	1.32	1.34	1.05	0.96	0.91	1.39 ± 0.1	0.98

<sup>a</sup> Means in ppb (1 ppb = 3.93 µg m<sup>-3</sup>) are only shown for months with at least 14 days of data. See Husain et al. (1998) for more details of the sample sets.  
<sup>b</sup> Means have been corrected for missing data using longterm average concentrations; sample collection averaged 286 days per year at Whiteface Mountain and 326 at Mayville.

Table 2  
Monthly mean total sulfur concentrations (ppb) at two sites in New York State

											Means	
	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1988–1994	1995–1997
<i>Whiteface Mountain</i>												
January	3.9		4.1	3.1		1.9	2.2	1.5	2.2	2.0	2.80	1.89
February	2.9		3.2	3.4		2.8	3.3	2.2	1.7	2.5	3.18	2.13
March	2.5		2.4	2.1		2.1	2.2	2.2	1.6	1.1	2.20	1.63
April	1.3		3.1	2.0		1.2	1.4	0.8	0.8	0.9	1.92	0.82
May	1.7	1.8	2.5	3.6			1.0	0.6	0.7	0.9	2.36	0.75
June	2.2	1.8	3.4	2.7		1.1	1.5	0.8	1.0	1.0	2.18	0.92
July	3.2	2.6	2.5	3.6	0.7	1.5	2.3	1.9	0.9	1.1	2.13	1.29
August	2.6	2.4	2.8	2.5	2.7	2.2	2.8	1.0	1.4	1.4	2.60	1.28
September		3.1	1.7	1.3	1.7	1.7	1.2	0.6	0.7	1.0	1.52	0.75
October		3.6	2.3	1.8	1.4	1.3	1.6	1.4	1.1	1.2	1.66	1.24
November		3.0	1.8	0.6	1.4	2.7	1.8	1.3	1.1	1.4	1.66	1.25
December		3.7	1.9		2.1	2.6	1.7	1.9	2.1	1.6	2.08	1.86
Means												
I quarter	3.05		3.24	2.85		2.26	2.57	1.95	1.84	1.86	2.73	1.88
II quarter	1.71	1.97	2.99	2.77		1.55	1.30	0.74	0.81	0.93	2.15	0.83
III quarter	2.89	2.70	2.33	2.47	1.71	1.79	2.11	1.17	0.99	1.16	2.08	1.11
IV quarter		3.43	2.00	1.50	1.62	2.19	1.69	1.52	1.44	1.39	1.80	1.45
Annual	2.25	2.67	2.64	2.40	2.05	1.95	1.92	1.35	1.27	1.34	2.19	1.32
<i>Mayville</i>												
January					11.89	8.00	10.03	5.72	8.82	6.54	9.97	7.03
February					10.73	12.10	10.08	7.80	7.22	6.75	10.97	7.26
March					7.68	12.31	8.28	4.77	9.36	4.39	9.42	6.17
April					5.97	7.98	6.85	2.74	4.49	4.65	6.93	3.96
May				8.11	8.30	5.18	5.88	5.47	4.40	3.29	6.86	4.39
June				7.53	7.69	6.53	5.78	4.18	5.75	5.25	6.88	5.06
July				8.48	7.48	6.28	7.63	4.24	4.58	4.82	7.46	4.54
August				8.70	5.73	7.34	6.18	4.39	5.93	5.38	6.99	5.23
September				7.78	6.60	6.08	5.50	4.48	4.26	5.37	6.49	4.70
October				9.28	6.82	7.90	7.75	6.58	6.02	6.80	7.94	6.47
November				8.91	7.85	8.98	5.68	6.42	5.80	5.57	7.85	5.93
December				9.89	8.67	7.94	11.18	6.32	7.66	6.84	9.42	6.94
Means												
I quarter					10.10	10.80	9.46	6.10	8.47	5.89	10.12	6.82
II quarter				7.52	7.32	6.56	6.17	4.13	4.88	4.40	6.89	4.47
III quarter				8.32	6.60	6.56	6.44	4.37	4.92	5.19	6.98	4.83
IV quarter				9.36	7.78	8.27	8.20	6.44	6.49	6.40	8.40	6.44
Annual				8.83	7.95	8.05	7.57	5.26	6.19	5.47	8.10	5.64

averaged 0.40 ppb at Whiteface Mountain compared to 1.04 ppb at Mayville. Third-quarter concentrations were a factor of 3.3 higher at Whiteface Mountain and a factor of 2.1 higher at Mayville. The patterns for 1995–1997 are similar, however, concentrations are lower by an average of 46% at Whiteface Mountain and 32% at Mayville.

### 3.2. Total sulfur

Monthly total sulfur concentrations from 1988 to 1997 are given in Table 2. Fig. 2 shows monthly  $\text{SO}_4$ ,  $\text{SO}_2$  and

$\text{S}_\text{T}$  for 1991–1994 at both sites. The trend observed for these years is representative of the remaining years as well. While  $\text{SO}_4$  is maximum in the third-quarter and minimum in the fourth, the pattern for  $\text{SO}_2$  is reversed. This is particularly pronounced at Mayville as  $\text{SO}_2$  concentrations for December through March are around 9 ppb or 2–3 ppb higher than any other month. The total S concentrations for December through March are around 10 ppb compared to a mean of 7.4 ppb for the other months (Table 2). Likewise at Whiteface Mountain,  $\text{S}_\text{T}$  is 35% higher in the first-quarter compared to the rest

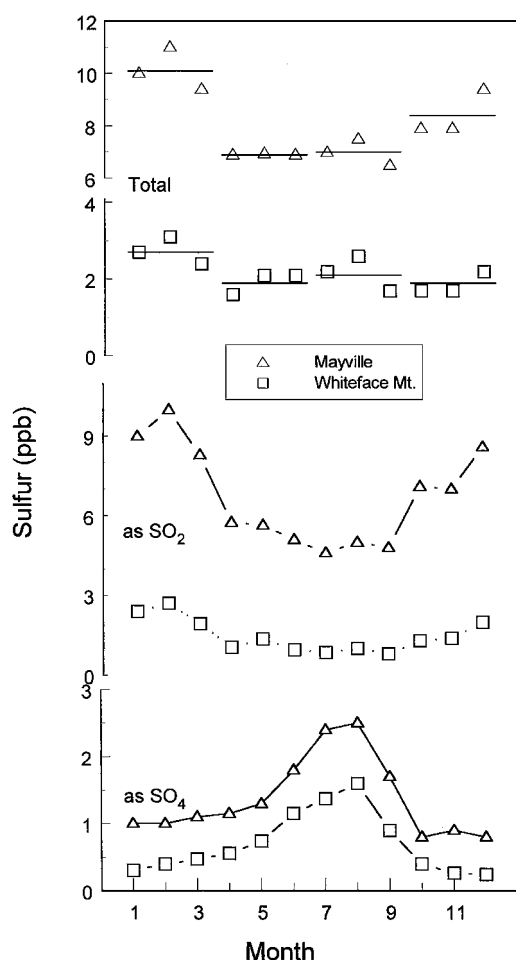


Fig. 2. Monthly mean  $\text{SO}_4$ ,  $\text{SO}_2$  and  $\text{S}_\text{T}$  concentrations at Mayville and Whiteface Mountain, NY, 1991–1994. The horizontal bars in the upper plots are quarterly mean  $\text{S}_\text{T}$ .

of the year, 2.7 ppb compared to  $2.0 \pm 0.1$  ppb. Prior to 1986  $\text{SO}_2$  emissions upwind in the Midwest during the first quarter were only around 10% higher than the remainder of the year (Knudson, 1986). Monthly emissions for recent years are not available. As both sites are high by the same factor, local space heating is probably not a major factor. The proportion of air from different directions, based on trajectories, does not vary much season to season at these sites (Husain and Dutkiewicz, 1990) so this cannot account for these differences. Air mass speeds derived from the air trajectories reaching the sites are highest in the first- and fourth-quarters,  $30 \text{ km h}^{-1}$  compared to the second- and third-quarters,  $27 \text{ km h}^{-1}$ . While faster transport may contribute to lower total dry deposition of  $\text{SO}_2$  and thus to the higher total S in the first-quarter, this alone cannot account for the difference since air mass speeds in the fourth-quarter are similar to those in the first-quarter, but total S in the

second through fourth-quarters is essentially unchanged. Perhaps, this observation is caused by lower mixing height in the boundary layer in winter which would tend to concentrate emissions more near the surface. During the remainder of the year there is little seasonal variation in  $\text{S}_\text{T}$  suggesting that transport parameters remain relatively constant, however,  $\text{SO}_4$  concentrations at both sites are maximum in the third-quarter when the oxidation rate of  $\text{SO}_2$  should also be maximum. For example, at Whiteface Mountain between October through February 89% of the S is present as  $\text{SO}_2$  compared to 50% during May to August. At Mayville the differences are not as great; 91% of S as  $\text{SO}_2$  during October through February compared to 73% during May to August. This is as expected since Mayville is much closer to the primary emission regions compared to Whiteface Mountain so, on average, less oxidation of  $\text{SO}_2$  can occur.

Between 1991 and 1994  $\text{S}_\text{T}$  at Mayville averaged 8.1 ppb compared to 2.0 ppb at Whiteface Mountain. At both sites  $\text{S}_\text{T}$  decreased by 35% in 1995 and has remained fairly constant through 1997. Thus, the changes in concentrations that were observed for  $\text{SO}_4$  in Table 1 are mirrored in  $\text{S}_\text{T}$ . We explore the relationship with regional  $\text{SO}_2$  emissions in the next section.

#### 4. Discussion

Husain et al. (1998) demonstrated a linear relationship between annual  $\text{SO}_4$  concentrations at Mayville and Whiteface Mountain and Midwest  $\text{SO}_2$  emissions. Air trajectories have been used earlier to relate  $\text{SO}_4$  concentrations at these sites to specific regional emissions (Parekh and Husain, 1982; Husain and Dutkiewicz, 1990). Here we evaluate the relationship between  $\text{SO}_4$  and  $\text{S}_\text{T}$  concentration and regional  $\text{SO}_2$  emissions further by using air trajectories to more specifically consider only the air that has passed through the Midwest and by expanding the source region to include contributions from southern Ontario.

##### 4.1. Relationship with air mass direction

We use the twelve  $30^\circ$  sectors shown in Fig. 1 to define the transport direction at each site. They are numbered clockwise with 1 being from due north to  $30^\circ$  east of north as shown in Fig. 1. For the  $i$ th day the fraction of the trajectory that passed through each sector was estimated and the results for the four trajectories combined to give the sector fraction for each day ( $f_{ij}$ ). A more detailed description can be found in Parekh and Husain (1982). By multiplying  $f_{ij}$  times the concentration ( $C_i$ ) the contribution of the  $\text{SO}_4$  concentration from each sector was approximated ( $C_{ij}$ ). By summing these contributions over a statistically significant time period (quarterly or annual basis) a mean concentration associated with each

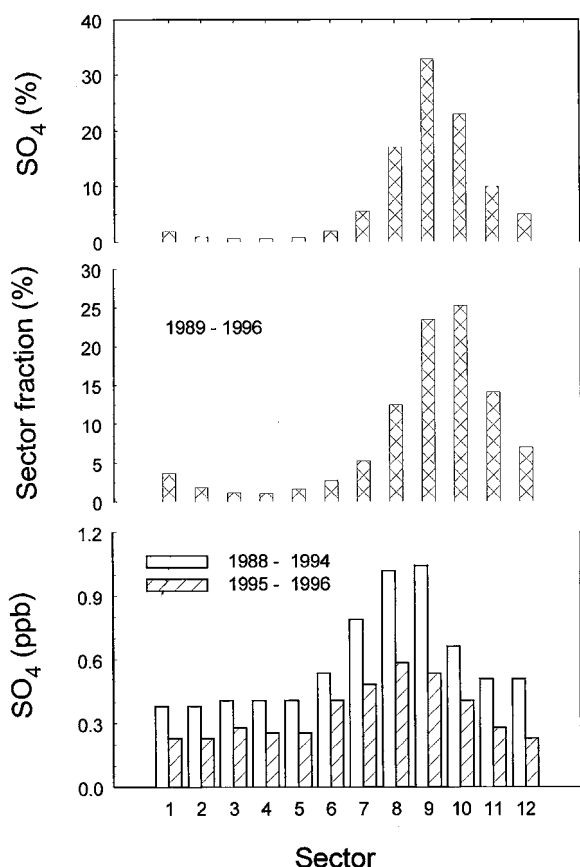


Fig. 3. Annual mean SO<sub>4</sub> concentration as a function of the 12 sectors for 1988 through 1994 and 1995 through 1996 at Whiteface Mountain, NY (lower panel), the fraction of time air masses were associated with each of the 12 sectors on an annual basis (middle panel), and the percentage of the annual average SO<sub>4</sub> attributable to each of the 12 sectors (upper panel).

sector direction is obtained (Husain and Dutkiewicz, 1990). As an example, Fig. 3 compares SO<sub>4</sub> concentrations at Whiteface Mountain for the 12 sector directions averaged from 1988–1994 to those averaged for 1995–1996. As SO<sub>4</sub> concentrations at these sites have varied little through 1994, averages for 1988 to 1994 are adequate to characterize conditions prior to implementation of reductions called for by the 1990 Clear Air Act. The highest concentrations are associated with sectors 8 and 9. The means for 1988–1994 was 1.0 ppb for both sectors compared to 0.58 and 0.53 ppb, respectively for 1995–1996. During both periods, concentrations for sectors 1 through 6, 11 and 12, are consistently lower by a factor of two or more. Sector 8 and 9 approximately subtend the Midwest emission region as shown in Fig. 1. The Midwest sector SO<sub>4</sub> (SO<sub>4MW</sub>) concentration of 0.55 ppb for 1995–1996 is 50% lower than that for 1981–1994, 1.09 ppb. This is in excellent agreement with

the 49% obtained with the annual means (Husain et al., 1998). Fig. 3 also shows the fraction of time air arrives from each sector and the fraction of total SO<sub>4</sub> associated with each sector (%C<sub>j</sub>) at Whiteface Mountain. Although SO<sub>4</sub> concentrations are much lower in 1995 and 1996 compared to the long-term means, there was no significant difference in either the fraction of air from each sector or the fraction of SO<sub>4</sub> between the 1988–1994 and 1995–1996. Thus, the means for the entire period are shown in Fig. 3. Since the air flow pattern for 1995 and 1996 is not significantly different from any other year, meteorologic differences contribute little to the large decreases in SO<sub>4</sub> concentrations reported. The Midwest sectors in Fig. 3 represent 50% of the annual average SO<sub>4</sub> with 33% coming from sector 9 alone. Sectors 10 and 11 account for most of the remaining contributions with 24 and 10%, respectively.

Mayville is much closer to Midwestern emissions and here sectors 7–10 best define the region. The highest concentrations are associated with air from sector 7, annual mean of 1.96 ppb for 1988–1994 compared to 1.53 ppb for 1995–1996. At Mayville, sector 10 represents the predominant direction for air masses, 19% of the time and sector 9 is only slightly lower at 17%. Sectors 1–6 contribute little, only 2.6–5% of the air masses. Concentrations of SO<sub>4</sub> are also lower, mean of 1.2 ppb between 1988 and 1994 and 1.06 ppb for 1995–1996.

Fig. 4 shows time series plots of mean annual SO<sub>4</sub> concentrations through 1997 and SO<sub>4MW</sub> based on air trajectory analysis through 1996 at both sites. At Whiteface Mountain, SO<sub>4MW</sub> averaged 46% higher than the all sector mean while at Mayville SO<sub>4MW</sub> averaged 14% higher than the mean. At both sites SO<sub>4</sub> concentration decreased slowly between 1980 and 1994 but there was a sharp decrease between 1994 and 1995, 28% at Mayville and 38% at Whiteface Mountain. This trend was mirrored in SO<sub>4MW</sub>. Fig. 5 shows scatter plots and linear regression lines between SO<sub>4MW</sub> and SO<sub>4</sub> at the two sites. At Whiteface Mountain there is a good linear fit,  $r^2 = 0.82$  and the intercept,  $0.14 \pm 0.08$ , is not significantly different from zero at the 90% confidence level. At Mayville there is also a good regression fit,  $r^2 = 0.86$  and the intercept,  $0.11 \pm 0.16$ , is again not significantly different from zero. Thus, with the exception of a scaling factor, 0.88 at Mayville and 0.67 at Whiteface Mountain, SO<sub>4</sub> and SO<sub>4MW</sub> concentrations will yield the same trends so only the data from all sectors will be used in the discussion below.

#### 4.2. Relationship with upwind SO<sub>2</sub> emissions

Husain et al. (1998) showed that the trends in SO<sub>4</sub> at these sites generally followed that of the emissions in the Midwest. The total SO<sub>2</sub> emissions from the Midwest states as defined in Husain et al. (1998); MN, WI, IL, IN, MI, OH, WV, KY, and western PA (WPA); but expressed

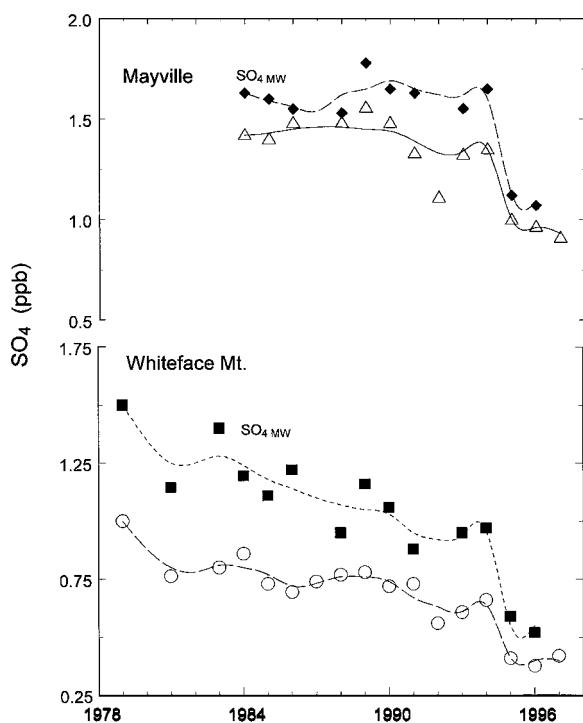


Fig. 4. Time series showing annual mean  $\text{SO}_4$  concentrations through 1997 and  $\text{SO}_{4\text{MW}}$  concentration at Whiteface Mountain and Mayville through 1996. The curves are the result of a cubic splines drawn through moving averages and are only added to aid the eye.

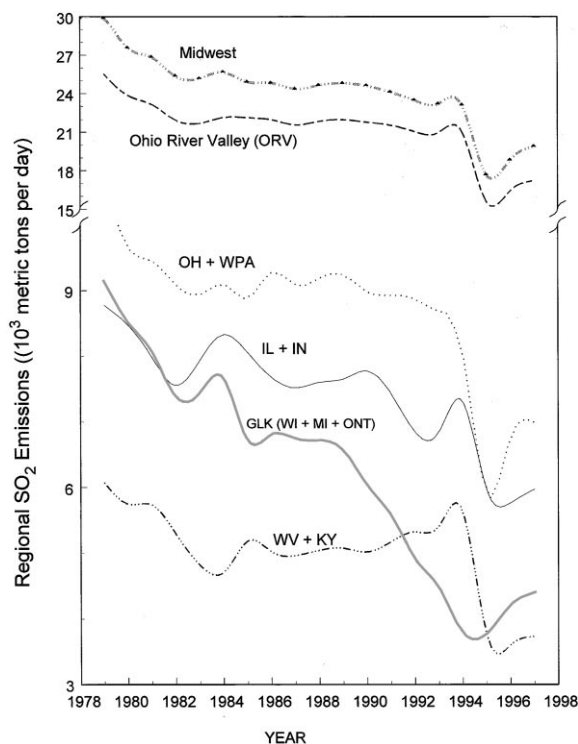


Fig. 6. Time series showing trends in  $\text{SO}_2$  emissions for the Midwestern States (OH, IN, IL, KY, WV, Western PA, MI, and WI), the Ohio River Valley (ORV) and the Great Lakes (GLK (WI + MI + ONT)). Sub-regions of the ORV are also shown, as defined in the text.

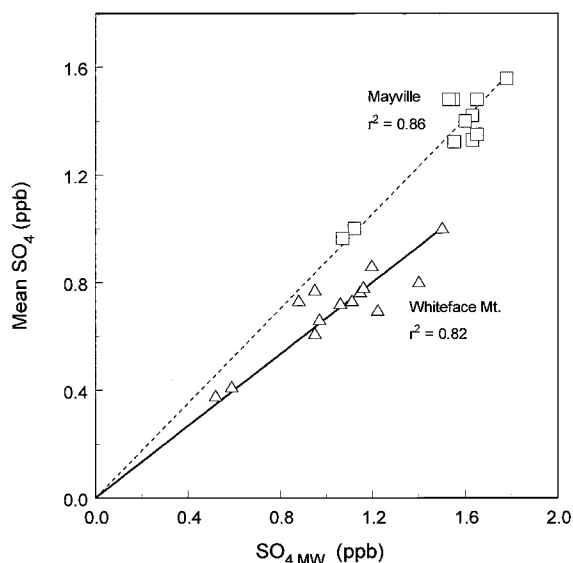


Fig. 5. Scatter plots of  $\text{SO}_4$  concentrations versus  $\text{SO}_{4\text{MW}}$  at Mayville and Whiteface Mountain. The lines are the result of linear regressions as explained in the text.

as daily average emissions, are shown in Fig. 6. We have obtained updated statewide  $\text{SO}_2$  emissions from 1990 to 1996 relative to the regional emissions used in Husain et al. (1998). As a consequence, emissions from 1990 to 1993 and 1995 in Fig. 6 are increased by 2% or less while those for 1994 are 3.1% higher (Thomas McMullen, USEPA, personal communication). The only significant change is that 1996 emissions have been increased by 26%. The large difference is due to the fact that the preliminary value used earlier was mistakenly for electric utilities only. Between 1982 and 1994 emissions decreased by  $\sim 1\%$  per year, but a large decrease occurred in 1995 due to implementations of provisions of the 1990 Clean Air Act. Using 1985 as the reference year,  $\text{SO}_2$  emissions for the Midwest were 29% lower in 1995 and 25% lower in 1996. The annual mean  $\text{SO}_4$  and  $\text{SO}_{4\text{MW}}$  in Fig. 4 generally follow the trend in Midwest  $\text{SO}_2$  emissions in Fig. 6.

Fig. 7A shows a scatter plot of annual mean  $\text{SO}_4$  at Whiteface Mountain versus Midwest emissions after Fig. 3 of Husain et al. (1998) but with the updated emissions. The best linear fit to the data (not shown) has  $r^2 = 0.90$ , but the line has a significant negative intercept,



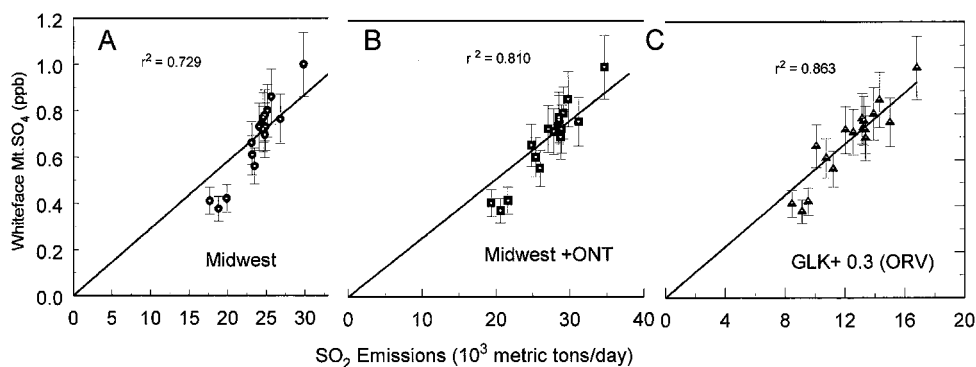


Fig. 7. Scatter plot of annual mean  $\text{SO}_4$  concentrations at Whiteface Mountain, NY versus Midwest  $\text{SO}_2$  emissions (A), Midwest + ONT emissions (B) and GLK + 0.3 ORV emissions (C) as explained in the text. The lines and regression coefficient are the result of linear regressions with the intercept set to 0.

$Y = -0.057(\pm 0.16) + 0.052(\pm 0.1)X$ . If the regression is forced to pass through the origin, as shown in Fig. 7A, then  $r^2 = 0.73$ . Considering the variability that may occur in meteorologic conditions and the uncertainties in the emissions, the fit is still good, however, the trends in Fig. 7A suggests that  $\text{SO}_4$  concentrations at Whiteface Mountain are decreasing faster than upwind emissions or the emission used do not completely describe the sources influencing this site. From the data shown in Fig. 1,  $\text{SO}_2$  emissions from Ontario Province in Canada (ONT) decreased more between 1985 and 1995 than any of the Midwestern States. And while the emissions are small compared to the states of OH, IL or IN, ONT is closer and directly in the path of prevailing air masses reaching Whiteface Mountain so emissions from this region may significantly affect  $\text{SO}_4$  concentrations at Whiteface Mountain. The emissions in Fig. 7B include Ontario's,  $\sim 10$  to 14% of the total. The resulting regression yields a superior correlation,  $r^2 = 0.80$  with zero intercept. Taking into account the uncertainties shown, Fig. 7B is a reasonable representation of the data although the data with the lowest emissions from the most recent years are all below the regression line.

The wind pattern influencing Whiteface Mountain is skewed toward the west and northwest (Fig. 3). Since  $\text{SO}_2$  is oxidized very slowly, the relationship between the emissions and  $\text{SO}_4$  concentrations depend on the distance. To study this relationship, the emissions have been subdivided into ORV (OH, IN, IL, WV, WPA, and KY) and GLK (ONT, MI, and WI). The ORV emissions (Fig. 6) were further divided into three sub regions: OH + WPA; IL + IN; and WV + KY. The trends for the three sub-regions are very similar and cannot really be distinguished one from another. This indicates that changes have generally been fairly homogeneous over the region and it is best to treat these emissions with the combined ORV profile shown in Fig. 6. The GLK emissions in 1979 were roughly one-third of these in ORV.

Emissions from the ORV decreased rather slowly until 1995. On the other hand, GLK emissions have decreased relatively rapidly. Thus, in 1985 ORV emission were a factor of 3.3 times larger than GLK, while in 1994 it was larger by a factor of 5.5. We can take advantage of the very different time trends for these two regions to fine tune the relationship between emissions and downwind  $\text{SO}_4$  concentrations. Let us assume that the true  $\text{SO}_2$  emission sources influencing our sites ( $[\text{SO}_2]$ ) is a linear combination of the GLK and ORV source terms.

$$[\text{SO}_{2a,b}] = a[\text{SO}_{2\text{GLK}}] + b[\text{SO}_{2\text{ORV}}]. \quad (1)$$

Since the GLK region is close and directly upwind of Whiteface Mountain, we set  $a = 1$  and allowed  $b$  to vary between 0 and 1 to obtain the best regression fit between  $\text{SO}_4$  and  $[\text{SO}_2]$  that passes through zero. Eq. (1) allows the ORV term to be scaled in a simple empirical way to compensate for the effect of air mass transport and the removal of S species. The best fit was obtained with  $b = 0.3$ ,  $r^2 = 0.86$ . This combination is shown in Fig. 7C. In this case more of the data fall within the 14% error bars. For comparison, the regressions with GLK emissions alone yielded  $r^2 = 0.68$  and the regression with ORV emissions alone yielded  $r^2 = 0.73$ . Thus, neither source regions by itself is adequate to represent the 19 yr trend at Whiteface Mountain. The 0.3 scaling factor for ORV at Whiteface Mountain makes sense since the bulk of the ORV sources are more distant than those in GLK, and the predominant direction of air flow reaching Whiteface Mountain (Fig. 3) is from sectors 9 and 10 (west and northwest). However, at Whiteface Mountain episodic high  $\text{SO}_4$  concentrations (daily concentrations  $> 10 \mu\text{g m}^{-3}$ ) are invariably associated with air that has passed through the ORV. The regression with  $\text{SO}_2$  emissions represented by  $a = 1$  and  $b = 0.3$  in Eq. (1) is a very good fit to the  $\text{SO}_4$  concentrations and suggest a direct one to one relationship between  $\text{SO}_4$  concentration at

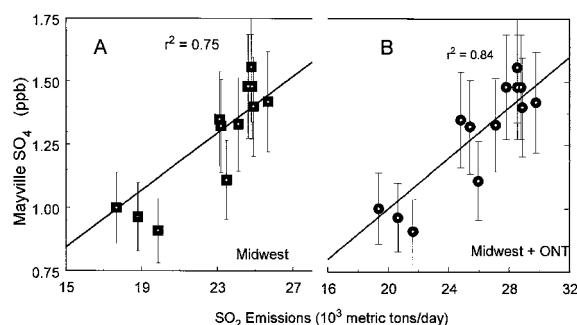


Fig. 8. Same as Figs. 7(A) and (B) except using annual mean  $\text{SO}_4$  concentration from Mayville, NY.

Whiteface Mountain and upwind  $\text{SO}_2$  emissions. Although the ORV source term has been reduced by a factor of 0.3, it is so much larger than the GLK term that the net result is that each region contributes roughly equal contributions to the  $\text{SO}_4$  at Whiteface Mountain, ORV = 51% and GLK = 49%. Since the GLK component (1995) consists of ONT = 45%, MI = 33%, and WI = 22%,  $\text{SO}_2$  emission from Midwestern states account for 78% of the  $\text{SO}_4$  at Whiteface Mountain and ONT sources account for the remaining 22%. This is similar to the results obtained earlier from air trajectories and elemental ratios (Husain and Dutkiewicz, 1990).

Fig. 8 shows a scatter plot of  $\text{SO}_4$  concentration at Mayville versus Midwest and Midwest + ONT  $\text{SO}_2$  emissions. The lines are the best linear regressions passing through zero. The regression that includes emissions from ONT is significantly better than the one that only includes the Midwestern states even though ONT only contributes around 10% to the total emissions. The emissions for Midwest + ONT are equivalent to ORV + GLK ( $a = b = 1$ ). If we apply Eq. (1) to the emissions and allow  $b$  to vary no other combination of ORV and GLK emissions yielded a better fit than the straight sum of Midwest + ONT shown in Fig. 8B. Since the Midwest is directly upwind from Mayville, this is not surprising. Fig. 8 demonstrates a direct one to one relationship between  $\text{SO}_4$  concentration at Mayville and reductions in upwind emissions.

The linear regressions in Figs. 7C and 8B imply that the ratios of  $\text{SO}_4$  concentration to the upwind regional emission strength at each site is a constant. In all further discussion regional  $\text{SO}_2$  emissions shall refer to GLK + ORV at Mayville and GLK + 0.3\*ORV at Whiteface Mountain. The mean and standard deviation of the  $\text{SO}_4/\text{SO}_2$  and  $\text{S}_\text{T}/\text{SO}_2$  emission ratio at the sites are summarized in Table 3. At Whiteface Mountain the  $\text{SO}_4/\text{SO}_2$  emission ratio has a standard deviation of only  $\pm 11.5\%$  over the 19 yr and the  $\text{S}_\text{T}/\text{SO}_2$  ratio is also highly stable as the standard deviation is only  $\pm 13.8\%$ . The corresponding ratios at Mayville show even less deviation with standard deviations of 7.4 and 8.5%, respectively. The net result of the small deviations in these ratios is that they can be used to predict the effect that future changes in regional emissions will have on the sulfur burden at these sites. At Mayville, the best linear fit with  $\text{SO}_4$  concentration was obtained by simply summing upwind emissions, GLK + ORV. While a reasonable fit was obtained for the  $\text{SO}_4$  concentrations at Whiteface Mountain using the same emissions (Fig. 7B), the best fit was obtained if the ORV emissions were scaled by 0.3 relative to those in the GLK. While this demonstrates the direct proportion between emissions and downwind  $\text{SO}_4$  concentrations, the ratios of  $\text{SO}_4$  and  $\text{S}_\text{T}$  concentrations to upwind emissions for Mayville and Whiteface Mountain in Table 3 are not directly comparable since a different source term was needed at Whiteface Mountain to compensate for transport and removal of S species. However, it may be possible to use  $\text{SO}_4$  and  $\text{S}_\text{T}$  data from a network of carefully chosen sites over northeast North America to expand this result to be applicable over a much larger region.

While a linear relationship between  $\text{SO}_2$  emissions and  $\text{SO}_4$  deposition is expected for the gas-phase pathway for  $\text{SO}_2$  oxidation to  $\text{SO}_4$ , non-linearity in the aqueous-phase channel have been predicted in environments where oxidants are limited. Aqueous-phase oxidation though more sporadic than gas-phase oxidation is much more rapid and oxidizes significant amounts of  $\text{SO}_2$ . Clouds associated with large frontal systems at Whiteface Mountain have been shown to have up to 60% of the  $\text{SO}_4$  in the cloud water originating from aqueous-phase oxidation (Husain et al., 1991; Dutkiewicz et al., 1995).

Table 3  
Mean ratios of  $\text{SO}_4$ , and total sulfur at sites in New York<sup>a</sup> to upwind  $\text{SO}_2$  emissions

Site	$\text{SO}_4/\text{SO}_2$ Emissions <sup>b</sup> ppb/ $10^5$ metric tons/day $\pm 1$ sigma ( $\pm 1$ sigma %)	$\text{S}_\text{T}/\text{SO}_2$ Emissions <sup>b</sup>
Mayville	$0.50 \pm 0.04$ ( $\pm 7.4\%$ )	$2.97 \pm 0.25$ ( $\pm 8.5\%$ )
Whiteface Mountain	$0.55 \pm 0.06$ ( $\pm 11.5\%$ )	$1.77 \pm 0.25$ ( $\pm 13.8\%$ )

<sup>a</sup> Means ratios with  $\text{SO}_4$  are for 1984–1997 at Mayville and 1979–1997 at Whiteface Mountain while mean ratios with  $\text{S}_\text{T}$  are for 1992–1997 and 1988–1997, respectively.

<sup>b</sup> For Mayville emissions = ORV + GLK, while for Whiteface Mountain emissions = GLK + 0.3 ORV.

McHenry and Dennis (1994) used a Comprehensive Sulfate Tracking Model to apportion aerosol production in northeastern North America and found that 60% of the  $\text{SO}_4$  was produced from aqueous-phase oxidation and only 40% from gas-phase. In a recent simulation for the Northeast, Wojcik and Chang (1997) found 70.4% of the aerosol  $\text{SO}_4$  in the domain came from aqueous-phase oxidation and only 29.6% from gas-phase oxidation. Models predict that this channel is the dominant pathway for  $\text{SO}_2$  oxidation in the region. If this is indeed the case, the results reported here suggests that any non-linearity due to the aqueous-phase oxidation in the Northeast domain must not be significant.

## 5. Summary and conclusions

$\text{SO}_4$  concentrations were measured daily at Whiteface Mountain from 1979 to 1997 and 530 km upwind at Mayville from 1984 to 1997. The concentrations changed little before 1994 but decreased sharply in 1995 and 1996. Variations in  $\text{SO}_4$  concentrations reflected the changes in  $\text{SO}_2$  emissions upwind. Relationship between changes in regional emissions and the concentrations were investigated using air trajectories. No measureable change in the directions of air flow or precipitation occurred in 1995 or 1996 relative to earlier years. Yet the  $\text{SO}_4$  contributed by the Midwest emissions was lower by 50% at Whiteface Mountain and 28% at Mayville during 1995–1996 compared to 1981–1991. The  $\text{SO}_2$  emissions in the Midwest decreased by  $\sim 30\%$  in 1995–1996, compared to 1981–1991. The more rapid decrease,  $\sim 50\%$  in  $\text{SO}_4$  concentration at Whiteface Mountain is explained in terms of relatively sharper decrease in  $\text{SO}_2$  emissions in Ontario. We estimate that half of the  $\text{SO}_4$  at Whiteface Mountain originates from sources along the Ohio River Valley and half from sources along the Great Lakes and that sources in Ontario contribute 22% of the total  $\text{SO}_4$ . At Mayville,  $\text{SO}_2$  emission sources in Ontario have less impact on  $\text{SO}_4$  concentration, 9% during 1995. At both sites a good linear fit with zero intercept was obtained between  $\text{SO}_4$  concentration and upwind  $\text{SO}_2$  emissions. These results in conjunction with those in Husain et al. (1998) provide compelling evidence of a direct one-to-one linear relationship between reductions in  $\text{SO}_2$  emissions and decreases in downwind concentrations of  $\text{SO}_4$ .

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## References

- Brook, J.R., Wiebe, A.H., Woodhouse, S.A., Audette, C.V., Dann, T.F., Callaghan, S., Piechowski, M., Dabek-Zlotorzynska, E., Dlughy, J.F., 1997. Temporal and spatial relationships in fine particle strong acidity, sulphate,  $\text{PM}_{10}$ , and  $\text{PM}_{2.5}$  across multiple Canadian locations. *Atmospheric Environment* 31, 4223–4236.
- Draxler, R.R., 1992. Hybrid single particle Lagrangian integrated trajectories (HY-SPLIT): Version 3.0 – Users Guide and model description. NOAA Technical Memorandum ERL-ARL-195, Air Resources laboratory, Silver Springs, MD.
- Dutkiewicz, V.A., Burkhard, E.G., Husain, L., 1995. Availability of  $\text{H}_2\text{O}_2$  for oxidation of  $\text{SO}_2$  in clouds in the northeastern United States. *Atmospheric Environment* 29, 3281–3292.
- Environment Canada, 1995. The Eastern Canada acid rain control program 1994, <http://www.ec.gc.ca/pdb/can-us/acidrn-e.pdf>.
- Environment Canada, 1997. 1996 Annual Report on the Federal-Provincial Agreements for the Eastern Canada Acid Rain Program. <http://www.ec.gc.ca/pdb/can-us/easteg97.pdf>.
- Hefter, J.L., 1983. Branching Atmospheric Trajectory (BAT) Model, NOAA Technical Memorandum ERLARL-121. Air Resources Laboratory, Rockville, Maryland.
- Husain, L., Dutkiewicz, V.A., 1990. A long-term (1975–1988) study of atmospheric  $\text{SO}_4$ : regional contributions and concentration trends. *Atmospheric Environment* 24A, 1175–1187.
- Husain, L., Webber, J.S., Canelli, E., Dutkiewicz, V.A., Halstead, J.A., 1984. Mn/V ratio as a tracer of aerosol sulfate transport. *Atmospheric Environment* 18, 1059–1071.
- Husain, L., Dutkiewicz, V.A., Hussain, M.M., Khwaja, H.A., Burkhard, E.G., Mehmood, G., Parekh, P.P., Canelli, E., 1991. A study of heterogeneous oxidation of  $\text{SO}_2$  in summer clouds. *Journal of Geophysical Research* 96 (D10), 18,789–18,806.
- Husain, L., Dutkiewicz, V.A., Das, M., 1998. Evidence for decrease in atmospheric sulfur burden in the eastern United States caused by reductions in  $\text{SO}_2$  emissions. *Geophysical Research Letters* 25, 967–970.
- McHenry, J.N., Dennis, R.L., 1994. The relative importance of oxidation pathways and clouds to atmospheric ambient sulfate production as predicted by the Regional Acid Deposition Model. *Journal of Applied Meteorology* 30, 890–905.
- Knudson, D.A., 1986. Estimated monthly emissions of  $\text{SO}_2$  and oxides of nitrogen for the contiguous 48 states, Vol I, Argonne National Laboratory, ANL/EES-MM-318.
- NAPAP, 1991. National Acid Precitation Program: Acidic Deposition: State of Science and Technology, Government Printing Office, Washington, DC.
- Newman, L., 1981. Atmospheric oxidation of sulfur dioxide: a review as viewed from power plant and smelter plume studies. *Atmospheric Environment* 15, 2231–2239.

- Pandis, S.N., Seinfeld, J.H., 1989. Sensitivity analysis of a chemical mechanism for aqueous-phase atmospheric chemistry. *Journal of Geophysical Research* 94, 1105–1126.
- Parekh, P.P., Husain, L., 1982. Ambient sulfate concentrations and wind flow patterns at Whiteface Mountain New York. *Geophysical Research Letters* 9, 79–82.
- USEPA, 1996. National Air Pollutant Emission Trends Report, 1990–1995, <http://epa.gov/oar/emtrnd/report96.html>.
- Wojcik, G.S., Chang, J.S., 1997. A re-evaluation of sulfur budgets, lifetimes, and scavenging ratios for eastern North America. *Journal of Atmospheric Chemistry* 26, 109–145.